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Fate of Resin Acids in Pulp Mill Secondary Treatment Systems

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Abstract

Profiles of resin and fatty acids (RFAs), COD, and aquatic toxicity were measured across the secondary treatment systems of three pulp mills. The RFAs sorb to suspended solids, principally fiber, and are partially removed through settling. An activated sludge system is more efficient in removing RFAs than is an aerated stabilization basin (ASB) because of its higher solids level. Dehydroabietic acid accounts for a significant fraction of the effluent toxicity in the two ASBs studied. The microorganisms in an ASB are unable to respond rapidly to an RFA spill, and effluent toxicity can be elevated for a prolonged period because of hydraulic mixing. The applicability of several laboratory studies to field situations is assessed.

Although many of the constituents that enter secondary treatment are toxic to aquatic organisms, a sizable fraction of these are removed during treatment (Morck *et al.* 2000). We reasoned that if the bulk of the effluent toxicity could be assigned to only a few compounds, then it might be possible to remove them in the process itself where the flow rates of the individual streams are relatively low. Resin acids occur naturally in softwood and have been repeatedly implicated as contributors to effluent toxicity (Leach *et al.* 1996; Leach and Thakore 1976; Liss *et al.* 1997; Peng and Roberts 2000; Zanella 1983). Of these, dehydroabietic acid (DHA) is of particular concern because it can be anerobically reduced to retene (Liss *et al.* 1997). We have determined the profiles of resin and fatty acids, COD, and aquatic toxicity across secondary treatment systems in order to evaluate their treatability and to establish their contribution to chronic and acute aquatic toxicity.

Experimental

The bulk of the study was conducted at Mill A, which is located in the southeastern US. Its production consists of 20% bleached hardwood, 30% bleached softwood, and 50% unbleached softwood. Its (4×10^6 m^3) aerated stabilization basin (ASB) contains four reactors with a total retention of 30-40 days. Samples were taken on three occasions in 1999, and once in 2000. During 1999, the first reactor was not aerated. The second and third reactors housed six and twelve 40-hp aerators, respectively. In early 2000, 1,200 hp of aeration was added to the first reactor and 360 hp was removed from the third; the samples collected in 2000 reflect this change. Grab samples were collected from the inlet and outlet of the first reactor, the outlets of the second and third, and from the final effluent. These samples are designated *1-in*, *1-out*, *2-out*, *3-out*, and *final*, respectively. Some of the samples were filtered through a Whatman 934AH glass fiber filter.

Mill B makes only bleached product from softwood, and samples were collected once in 2000. The 1.4×10^6 m^3 lagoon receives 2,850 hp of tapered aeration and is curtained into three zones, with 80% of the aerators being located in the first zone. Mill C makes bleached pulp and

its fiberline swings between hardwood and softwood production. Its activated sludge system (AST) has a retention time of 17 hours. Eight samples were collected semiweekly in 1994. Mills B and C are also located in the Southeastern US.

The resin and fatty acids determined were abietic, dehydroabietic, neoabietic, pimaric, isopimaric, sandracopimaric, palustric, oleic, and stearic acid, and are collectively designated as "RFA." Aqueous samples were extracted with diethyl ether and the RFAs determined by gc-fid. (NCASI, 1989). Microtox analyses were performed with a Microtox Model 500 Analyzer obtained from AZUR Environmental. *Ceriodaphnia dubia* assays were run in the final effluent of Mill A (amended on occasion with DHA) by Law Engineering and Environmental Services, Kennesaw, GA.

Results and Discussion

The long hydraulic residence time in the Mill A lagoon makes the concentration profiles along the lagoon difficult to interpret, since the input to the lagoon is not necessarily constant. The concentration of a compound at a given location reflects not just the various degradative and dissipative pathways, but also a varying input load. Figure 1 compares filtered and unfiltered RFA concentrations. Note that the difference between the two decreases along the lagoon, since the TSS decreases concurrently. Hence, a significant fraction of the RFA material is bound to solids and is probably removed through settling.

The inlet sample was taken from the inflow to the treatment system and the solids are mainly wood fiber. Consider the solids:water distribution at locations *1-out* and *2-out* in Figure 1. Values for the (dimensionless) fiber:water distribution coefficient, K_d, were identical at the two locations at 7,000 for the December 1999 samples; the corresponding values for March 2000 were 15,200 and 15,600 respectively. The partitioning of resin acids between inactivated aerobic biomass and water followed a linear isotherm (Hall and Liver 1996), with a much lower K_d of 300-1,100. Hence, our values are far too high to reflect simple partitioning to biomass. Hydrophobic compounds sorb strongly to the lignin in pulp fiber and fines (Severtson and Banerjee 1996, 2001), and it is likely that the resin acids are principally bound to fiber and fiber-derived fines rather than to microbial biomass at *1-out*. The fibers progressively settle out, and the resin acids in the unfiltered and filtered samples eventually converge. This is not to minimize the importance of sorption to biomass. However, if the fiber constitutes a significant fraction of the initial TSS, then the resin acids will substantially associate to and settle with the fiber.

COD and toxicity profiles are provided in Figure 2 and show that the toxicity decreases just after the bulk of the COD is removed. The chronic and acute toxicity profiles correlate only to the extent that both decrease just after the first reactor for the December sampling and within the first reactor for the March episode, which benefited from increased aeration. The level of aeration was increased before the March 2000 sampling, and this leads to an earlier drop in COD as compared to the December result. The toxicity is also reduced earlier in March, reflecting the removal of some of the toxicants. These results confirm that many of the compounds that induce acute toxicity are biologically degradable. However, the decrease in chronic toxicity is not as pronounced.

Profiles of DHA, RFA, and COD (all filtered) collected on two occasions are presented in Figure 3. The March results are unexceptional; all three constituents decrease in Reactor 1. The December results, however, show a DHA/RFA spike at the outfall of Reactor 1, which almost certainly originates from an earlier spill. Remarkably, the COD decreases smoothly, and the profile resembles those (not shown) collected on other occasions in 1999. Hence, the COD and RFAs must be removed through different mechanisms, at least in a spill situation. Since RFAs are among the more recalcitrant COD constituents, they are not degraded as rapidly and appear as a broad pulse. This possibility was suggested earlier (Werker and Hall 1999, 2000), who found in laboratory-scale work that microorganisms acclimated to resin acids were unable to degrade a shock load because of a long lag period. Hence, if a spike clears the front end of the lagoon where biological activity is most intense, it could travel through the system relatively unaffected. Figure 3 provides full-scale confirmation of Werker and Hall's laboratory findings.

It follows that if RFAs are spilled into the lagoon, their concentrations will be elevated until the spike is washed out. The Microtox EC_{50} of DHA-spiked final effluent (Mill A) was 3.7 ppm. In the absence of a spill, the effluent DHA averaged about 30% of this value as shown in Figure 4 for the May 1999, September 1999, and March 2000 samplings. For the December 1999 sampling, the effluent DHA was 3.8 ppm, and toxicity should be elevated not just for this period, but also for the considerable interval required for the spike to clear the lagoon. In other words, if plug flow conditions applied, then a high RFA concentration would be found in the effluent for a short period. Mixing lowers this concentration but lengthens the duration of elevated RFA levels in the effluent. The EC_{50} for reproduction to *C. dubia* measured in Mill A effluent was 2 ppm. A higher LC_{25} value of 6.6 ppm was reported earlier (O'Connor *et al.* 1992), but this test was run in well water where the contribution of other toxicants was absent. Hence, the final effluent DHA value is just below the LC_{50} threshold in the absence of a spill, and may exceed it for a prolonged period under upset conditions.

Roughly similar results were obtained for Mill B and are compared to those from Mill A in Table 1. A direct comparison of samples taken within the lagoon across the two mills is difficult, since the geometry and mixing characteristics are very different. Hence, only the influent and effluent results are considered. As with Mill A, the major drop occurred early in the system. Although the influent values were higher (on average) than those of Mill A, the final effluent concentrations were similar, indicating that the RFAs contribute significantly to effluent toxicity. As with Mill A, the DHA/RFA ratio increased from influent (0.21) to effluent (0.34), confirming the relative recalcitrance of DHA. A similar recalcitrance has been reported in a full-scale study (Zender *et al.* 1994).

Mill C alternated between softwood and hardwood production. The RFAs in the influent changed concomitantly, since they are generally absent in hardwood. Over the eight sampling occasions, the unfiltered DHA and RFA influent concentrations were 4 ± 2 and 30 ± 20 ppm, respectively; the corresponding effluent values were 0.2 ± 0.2 and 1 ± 1 ppm, respectively. The relatively high uncertainty results from the fiberline swing between hardwood and softwood. As before, the DHA/RFA ratio increased from the influent to the effluent, in this case, from 0.13 to 0.19. DHA decreases by 95% across the treatment system, as compared to 59 and 70% for Mills A and B, respectively. Although possible, it is unlikely that this increase is entirely due to improved biological action, since the efficiencies of ASTs and ASBs are similar for other constitu-

ents (Kemeny and Banerjee, 1997). The suspended solids levels in an AST are much higher than those in an ASB, and sorption and settling is expected to play a larger role in an AST. These results are consistent with the results of an earlier field study (Williams *et al.* 1997) where the degradation of radiolabeled oleic acid in an AST and an ASB was compared. Sorption was found to play a more important role for the AST, which suggests that resin acid toxicity should be less prevalent in an AST.

Our major conclusion is that RFAs in general, and DHA in particular, can be responsible for a significant fraction of the chronic effluent toxicity in ASBs. Their presence in the effluent of an AST should be smaller. They are only partially removed biologically, and association with fiber or biomass and subsequent settling represents an important removal pathway. If an RFA spill is large enough to traverse the front end of an ASB, which is the region of highest biological activity, then the spike can move through the lagoon since both biological activity and the TSS level will progressively decrease through the treatment system. The spike will broaden as it moves due to mixing in the lagoon and could elevate effluent toxicity until it washes out.

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Table 1: Comparison of DHA and RFA levels (ppm) across Mills A and B

	DHA_{in}	DHA_{out}	RFA_{in}	RFA_{out}
Mill A[1]	3.0	1.7	9.6	4.5
Mill B	8.0	2.4	39	7.1

[1]averaged over 4 sampling episodes

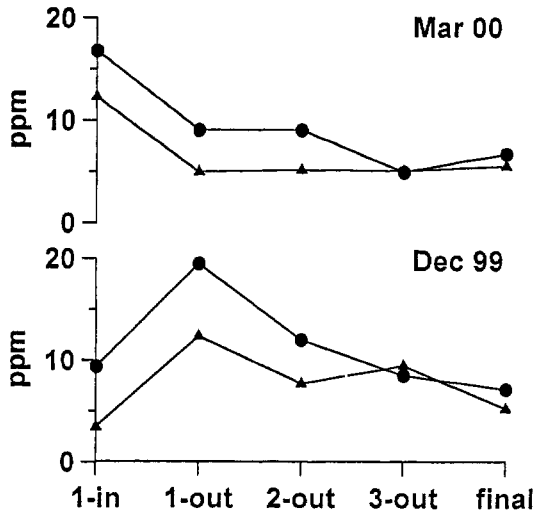

Figure 1: Filtered (triangles) and unfiltered (circles) RFA concentrations.

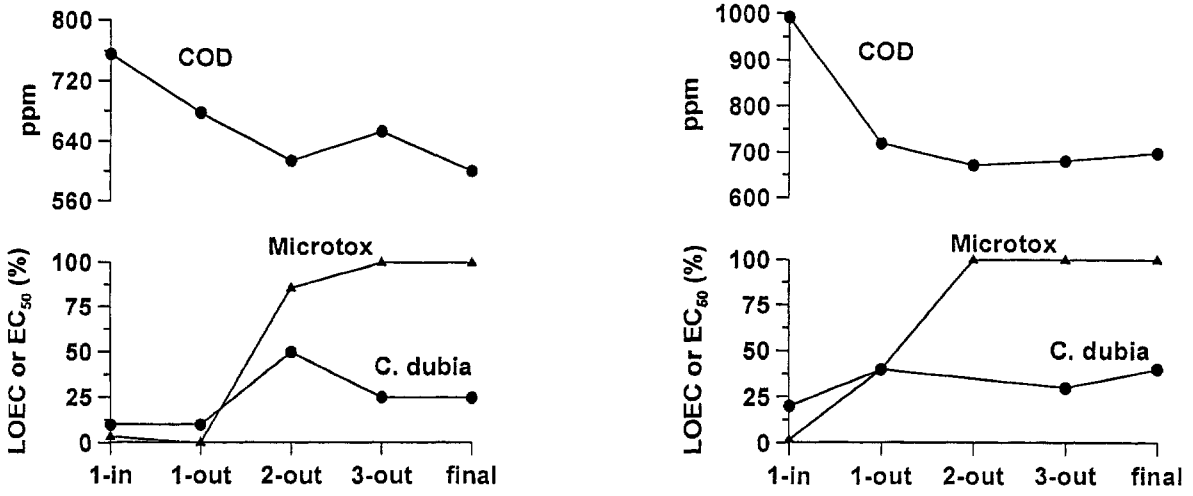

Figure 2: COD and toxicity profiles for samples collected in December 1999 (left) and March 2000 (right). EC_{50} and LOEC apply to the Microtox and *C. dubia*, respectively

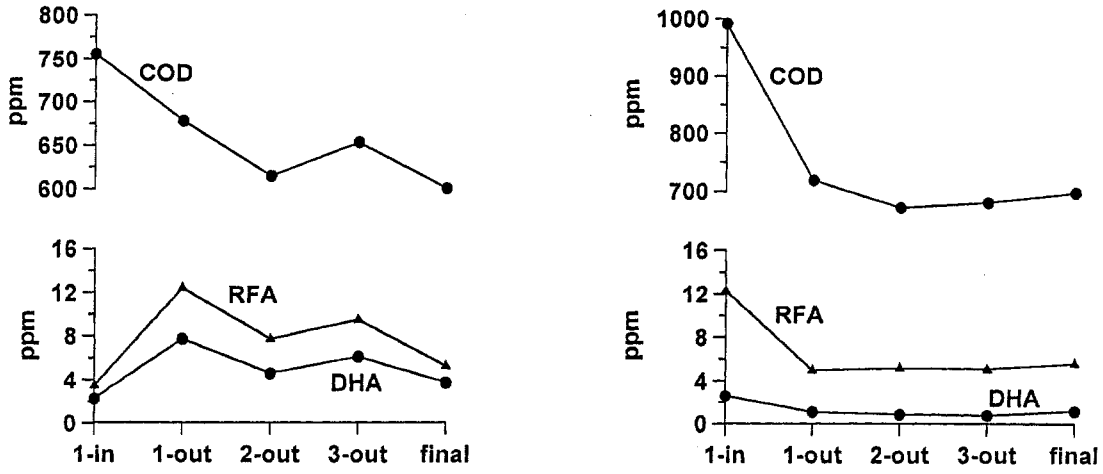

Figure 3: COD, RFA, and DHA profiles for samples collected in December 1999 (left) and March 2000 (right).

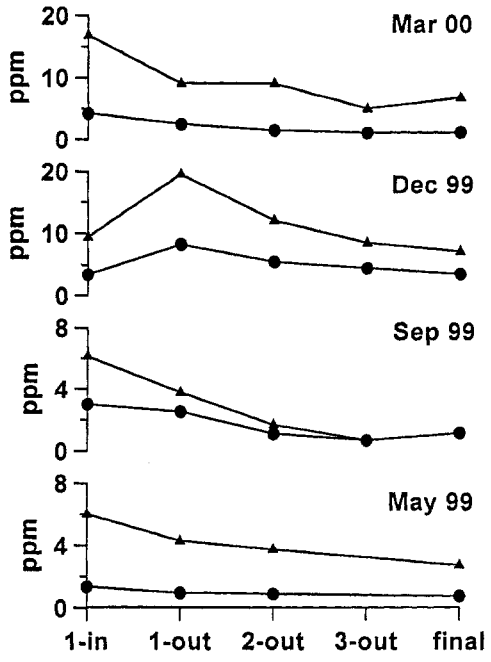

Figure 4: Total (unfiltered) RFA (triangles) and DHA (circles) profiles collected at various periods.